

# **Report for 2003DE30B: REMOVAL AND INACTIVATION OF WATER-BORNE VIRUSES USING PERMEABLE IRON BARRIERS**

## **Publications**

- Conference Proceedings:
  - You, Y.; J. Han, Liping Zhang, Pei C. Chiu, Yan Jin, 2006, Removal and Inactivation of Waterborne Viruses Using Zero-Valent Iron, in The 4th International Slow Sand and Alternative Biological Filtration Conference Proceedings, IWW Water Centre, Mulheim an der Ruhr, Germany, 8 pp.
  - Zhang, Liping. Poster Presentation October 21, 2005. Removal and Inactivation of Water-Borne Viruses Using Permeable Iron Barriers, In Proceedings of Fifth Delaware Water Policy Forum, University of Delaware, Newark, Delaware, p 17.  
<http://www.wr.udel.edu/publicservice/WaterForum2005/waterforum05.pdf>
  - Zhang, Liping, 2006, Removal and Inactivation of Viruses with Elemental Iron, in proceedings of the 231st American Chemical Society (ACS) National Meeting, Atlanta, GA.

## **Report Follows**

## **INTRODUCTION AND OBJECTIVES**

Microbial pathogens (bacteria, protozoa, and viruses) in drinking waters represent a serious public health problem. Sources of enteric pathogens in source water include septic tanks, landfills, sewage sludge application on land, and wastewater discharge and reuse (Yates, et al., 1985), as well as runoff and infiltration from animal waste-amended fields (McMurry et al., 1998). Among the different microbial pathogens, viruses are particularly problematic because they are highly mobile in soil and groundwater and difficult to remove by filtration due to their small size. Viruses were reported to be responsible for approximately 80% of disease outbreaks for which infectious agents were identifiable (Ryan et al., 2002). The U.S. EPA has promulgated Long Term 1 Enhanced Surface Water Treatment Rule (SWTR) and put forward Long Term 2 Enhanced SWTR (U.S. EPA, 2003) to set treatment requirements to reduce microbial contamination.

Chlorination is the most common process for water and wastewater disinfection. However, chlorine was shown to be less effective against viruses than bacteria (Payment and Armon, 1989, Bull et al., 1990). A recent study (You et al., 2005) demonstrated that in a flow-through column containing Fe(0), two bacteriophages, MS2 and  $\phi$ X174, were removed from artificial groundwater with an efficiency of 4-log (99.99%) in an initial pulse test, and more than 5-log (>99.999%) in the second pulse test after passage of 320 pore volumes of artificial groundwater. These authors suggested that the viruses might be removed by iron corrosion products, and that the improved efficiency over time might be due to continued formation of surface iron oxides through corrosion.

In the previous (FY2004) annual progress report to DWRC, we showed results of MS2 and  $\phi$ X174 removal by elemental iron after different treatments (as-received, acid-treated, and after anaerobic corrosion). The main findings were that iron as-received effectively removed MS2 and  $\phi$ X174 under the experimental conditions, and the removal was mostly due to inactivation rather than adsorption.  $\phi$ X174 was inactivated by both acid-treated iron and its corrosion products whereas MS2 was inactivated primarily by iron corrosion products.

X-ray diffraction (XRD) characterization of corroded iron demonstrated that magnetite ( $\text{Fe}_3\text{O}_4$ ) was the major oxidation product of anaerobic iron corrosion. We also measured aqueous Fe(II) in batch experiments with 1 g of acid-treated iron and observed increasing Fe(II) concentration over time. We decided to examine the effects of the two corrosion products individually on the removal of the two viruses.

The main objective of our study in 2005 was to evaluate the roles of Fe(0) itself and its anaerobic corrosion products, aqueous Fe(II) and magnetite ( $\text{Fe}_3\text{O}_4$ ), on the removal of  $\phi$ X174 and MS2 from water.

## **RESULTS TO DATE (FY04-FY05)**

In summary, our experiments show that Fe(0) itself had little effect on either of the MS2 or  $\phi$ X174 bacteriophage. Aqueous Fe(II) inactivated  $\phi$ X174 to a large extent but had little influence on MS2.  $\text{Fe}_3\text{O}_4$  adsorbed and inactivated both viruses, although  $\phi$ X174 appeared to be more susceptible to inactivation by  $\text{Fe}_3\text{O}_4$  than MS2. The results suggest

that it was the corrosion products, rather than Fe(0) itself, that were responsible for the observed virus removal and inactivation in Fe(0) systems.

Table 1 summarizes the main results to date, from both FY2004 and FY2005.

Table 1 Summary of batch results

Iron Sample	MS2		$\phi$ X174	
	Removal	BEX recovery	Removal	BEX recovery
1g Fe(0) as-received	93.2% in 4 hr	16.8%	99.5% in 4 hr	0.5%
1g Fe(0) treated with 0.5 M HCl	53.0% in 3 hr	80%	98.7% in 3 hr	1.9%
1g Fe(0) treated with 1 M HCl	No removal	N/A	90.8% in 3 hr	1.0%
1g Acid treated Fe(0) + 3mM citrate	N/A	N/A	No removal	N/A
0.5 mM Fe(II)	No removal	N/A	95.7 % in 12 min	N/A
Fe(II) at four conc.: 0.01, 0.03, 0.1, 0.3mM. Reaction time: 10 min	N/A	N/A	52.4% at 0.01mM 83.6% at 0.03mM 85.8% at 0.1 mM 91.7% at 0.3 mM	N/A
1g Corroded iron	99.4% in 3 hr	53.9%	99.9% in 3 hr	2.5%
1 g Fe <sub>3</sub> O <sub>4</sub>	99.6% in 3 hr	84.8%	99.9% in 3 hr	22.9%

#### PLAN FOR FY2006

The objectives and tasks for FY2006 will include (1) to elucidate the mechanisms involved in virus inactivation by aqueous Fe(II) and Fe<sub>3</sub>O<sub>4</sub>, and (2) to evaluate the effects of common constituents in natural waters, such as natural organic matter, on virus removal efficiency with Fe(0). The long-term goal is to better assess the feasibility and limitations of Fe(0) as a potential virus removal technology for water purification